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Boundary Lubrication—Revisited

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BOUNDARY LUBRICATION - REVISITED

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Summary

A review of the various lubrication regimes, with particular emphasis on boundary lubrication, is presented. The types of wear debris and extent of surface damage is illustrated for each regime. The role of boundary surface films along with their modes of formation and important physical properties are discussed. In addition, the effects of various operating parameters on friction and wear in the boundary lubrication regime are considered.

Introduction

The purpose of lubrication is to separate surfaces in relative motion by a material which has a low resistance to shear so that the surfaces do not sustain major damage. This low resistance material can be a variety of different species (e.g., adsorbed gases, chemical reaction films, liquids, solid lubricants, etc.).

Depending on the type of intervening film and its thickness, a number of lubrication regimes can be identified. A classical way of depicting some of these regimes is by use of the well known Stribeck curve (fig. 1). Stribeck (ref. 1) performed comprehensive experiments on journal bearings around 1900. He measured the coefficient of friction as a function of load, speed, and temperature. However, it was difficult to condense this data into usable form. Some years later, Hersey (ref. 2) performed similar experiments and devised a plotting format based on a dimensionless parameter. The Stribeck curve, or more appropriately, the Stribeck-Hersey curve takes the form of the coefficient of friction as a function of the viscosity (2), velocity (N), and load (P) parameter, ZN/P.

At high values of ZN/P which occur at high speeds, low loads, and at high viscosities, the surfaces are completely separated by a thick (>0.25 μm) (>10⁻⁵ in.) lubricant film. This is the area of hydrodynamic lubrication where friction is determined by the rheology of the lubricant. For nonconformal concentrated contacts where loads are high enough to cause elastic deformation of the surfaces and pressure-viscosity effects on the lubricant, another fluid film regime, elastohydrodynamic lubrication (EHD) can be identified. In this regime film thicknesses (h) may range from (0.025 to $2.5~\mu m$) (10⁻⁶ to 10^{-4} in.).

As film thickness becomes progressively thinner, surface interactions start taking place. This regime of increasing friction in which there is a combination of asperity interactions and fluid film effects is referred to as the mixed lubrication regime.

Finally, at low values of the ZN/P parameter, one enters the realm of boundary lubrication, the primary subject of this paper. This regime is characterized by the following (ref. 3):

1. It is a highly complex regime involving metallurgy, surface topography, physical and chemical adsorption, corrosion, catalysis, and reaction kinetics. 2. The most important aspect of this regime is the formation of protective surface films to minimize wear and surface damage.

3. The formation of these films is governed by the chemistry of both the film former as well as the surface and other environmental factors.

4. The effectiveness of these films in minimizing wear is determined by their physical properties which include: shear strength, thickness, surface adhesion, film cohesion, melting point or decomposition temperature, and solubility.

It is obvious that a concise definition of boundary lubrication is not possible. For the purposes of this paper, the following general definition will be used. Boundary lubrication is lubrication by a liquid under conditions where there is appreciable solid-solid interactions. Friction and wear are determined predominantly by interactions between the solid surfaces and between the surfaces and the liquid. The viscous properties of the liquid play little or no part in this process.

The purpose of this paper is to summarize the present knowledge about boundary lubrication. There is no intent to provide an exhaustive survey of the literature. A number of adequate surveys already exist (refs. 3 to 8).

Lubrication Regimes

Besides the Stribeck-Hersey curve (fig. 1) described in the introduction, an idealized plot of wear rate as a function of relative load can also delineate the various lubrication regimes as well as some wear transitions (fig. 2) (ref. 8).

Region OA

This region encompasses the regimes of hydrodynamic and elastohydrodynamic lubrication (EHD), the latter as point A is approached. Since there are no surface interactions in this region except for startup or shutdown, little or no wear occurs. This is excluding rolling element fatigue which can occur without surface interactions.

Region AX

Region AX is the mixed lubrication regime where surface interactions begin to occur at $\,A\,$ and become more prevalent as point $\,X\,$ is approached. Wear is low because there are still fluid film effects.

Region XY

This is the region of boundary lubrication. The degree of metal to metal contact and the wear rate increase as the load increases. Wear is mild and tends to be corrosive to the left of B and adhesive to the right of b. The location of B is quite variable and depends on the corrosivity of the lubricant formulation. For a noncorrosive lubricant, adhesive wear can occur at X. On the other hand, a corrosive additive can extend the boundary regime to Z^{1} before boundary film failure occurs.

Region YZ

This is the regime of severe wear where scuffing and scoring occur. Machinery cannot operate successfully in this region and, therefore, the loca-

tion of this transition point is quite important. At point λ , there is total surface failure and seizure occurs.

Wear Particles and Surface Damage

The types of wear particles and surface damage generated during these lubrication regimes has been reported by Reda, et al. (ref. 9). In that study, wear particles were generated in sliding steel contacts and were isolated by Ferrographic analysis (ref. 10). Basically, this technique involves pumping a quantity of used lubricant across a glass slide which sits on top of an electromagnet (fig. 3). The ferromagnetic wear particles are magnetically precipitated onto the slide and can then be observed microscopically. Surface damage can also be observed by microscopic examination.

Hydrodynamic and EHD Regimes

Since the surfaces are completely separated in these regimes, no wear or surface damage should be evident. This is the case with a featureless surface (fig. 4(a)) and only a few isolated wear particles (fig. 4(b)).

Mixed and Boundary Lubrication Regimes

These are mild wear regimes where penetration of the boundary film occurs.

This produces the surface damage as illustrated in figure 5(a). Wear parti- cles are generated in a thin surface layer that is continuously removed and reformed during the sliding process. In Ferrographic terminology the wear particles generated in these regimes are referred to as normal rubbing wear particles. These flake-like particles are released into the lubricant by an exfoliation or fatigue-like process. The rate of removal of this surface layer is less than its rate of formation. Wear occurs continuously but at a low rate.

These wear particles are arranged in strings by the magnetic field of the Ferrograph (fig. 5(b)). A scanning electron micrograph (fig. 6) (ref. 11) at a higher magnification illustrates their flake-like nature. Typically, for steel surfaces, these particles are 0.75 to 1.0 μ m in thickness with a major dimension of less than 15 μ m.

The transition from the EHD regime into the mixed and boundary regimes is dramatically illustrated by Ferrographic analysis (fig. 7) (ref. 12). In this figure the Ferrogram density is plotted as a function of the Λ ratio. Ferrogram density is a measure of the amount of wear particles. The Λ ratio is the ratio of the film thickness to the composite surface roughness. This data was generated by sliding steel balls of three different roughnesses against a sapphire plate. As can be seen, the amount of wear debris increases sharply at Λ values of one and below where surface interactions begin taking place. The comparable curve for the friction coefficient (f) as a function of the Λ ratio appear in figure 8 (ref. 12). Here the corresponding increase in the friction with increasing surface interactions is evident. This is analogous to the rising portion of the Stribeck-Hersey curve (fig. 1) in the mixed film regime.

Transition to Severe Wear

As load is increased, there is some point (Y) (fig. 2) where the rate of removal of the surface layer starts to exceed its rate of formation. A transition from mild to severe wear occurs. Surface damage becomes more extensive (fig. 9(a)). As the surface film starts to tail, much larger metallic wear particles (up to 150 μ m in major dimension) are formed (fig. 9(b)).

Mild Oxidative Wear

Under certain conditions a mild form of oxidative wear occurs. Here the majority of wear particles are iron oxide of the αFe_2O_3 type (hematite). The surfaces appear oxidized and grooved to depths of 20 μm (fig. 10(a)). The wear particles appear reddish-orange in reflected white light (fig. 10(b)).

Severe Oxidative Wear

As load is further increased, a transition from mild to severe oxidative wear occurs. The surfaces are now grooved to depths of $100~\mu m$ and black oxide appears on the surface (fig. 11(a)). The generation of black oxide particles consisting of γ -Fe₂0₃, Fe₃0₄ and Fe0 predominates (fig. 11(b)).

Both of these oxidative wear regimes are most commonly observed during unlubricated conditions. However, both regimes have been observed during lubricated sliding which is indicative of very poor, perhaps starved, lubrication.

Seizure

Finally, at very high loads, complete breakdown of the wear surface occurs. Considerable smearing and tearing of the surface is evident with grooving to 200 μm (fig. 12(a)). Free metallic particles having dimensions up to 1 mm are generated (fig. 12(b)).

Boundary Film Formation

As discussed in the introduction, the most important aspect of boundary lubrication is the formation of surface films (from additives or the lubricant itself) which will protect the contacting surfaces. Basically, there are three mechanisms of boundary film formation: physical adsorption, chemisorption and chemical reaction (ref. 13).

Physical Adsorption

Physical adsorption involves intermolecular forces analogous to those involved in condensation of vapors to liquids. Physical adsorption is usually rapid, reversible, and nonspecific. Energies involved in physical adsorption are in the range of heats of condensation. Physical adsorption may be monomolecular or multilayer. There is no electron transfer in this process. An idealized example of the physical adsorption of hexadecanol on an unreactive metal is shown in figure 13. Because of the weak bonding energies involved, physically adsorbed species are not very effective boundary lubricants.

Chemisorption

Chemisorption of a species on a surface is usually specific, may be rapid or slow and is not always reversible. Energies involved in chemisorption are large enough to imply that a chemical bond has formed (i.e., electron transfer has taken place). Chemisorption is a monomolecular process. It also may require an activation energy as opposed to physical adsorption which requires none. A species may be physically adsorbed at low temperatures and chemisorbed at higher temperatures. In addition, physical adsorption may occur on top of a chemisorbed film. An example of the chemisorption of stearic acid on an iron oxide surface to form iron stearate is illustrated in figure 14.

Chemical Reaction

Although chemisorbed films involves a chemical reaction, this section mainly deals with inorganic reaction products on surfaces. This process is also specific, may be rapid or slow (depending on temperature, reactivity and other conditions), and is irreversible. Films can be unlimited in thickness. An idealized example of a reacted film of iron sulfide on an iron surface is shown in figure 15.

Another chemical reaction of import to boundary lubrication is "friction polymer" formation. In 1958, Hermance and Egan (ref. 14) reported on the occurrence of organic deposits on electrical relay contacts and coined the term "friction polymer." Since that time many investigators have observed the presence of this material in lubricated contacts. Although little is known about its mode of formation or its chemical structure, it can, in some cases, act as a boundary lubricant (ref. 14). An example of "friction polymer" debris generated by a polyphenyl ether appears in figure 16 (ref. 15). A summary of the importance of friction polymers in lubricated contacts appears in reference 16.

Physical Properties of Boundary Films

The physical properties of boundary films that are important in determining their effectiveness in protecting surfaces include: melting or decomposition temperature, shear strength, thickness, surface adhesion, cohesion and solubility in the bulk lubricant.

Melting Point

The melting point of boundary films is probably the most common property which correlates with film failure. The literature is replete with such examples. Russell, et al., (ref. 17) reported friction transitions for copper lubricated with pure hydrocarbons. Friction data for two hydrocarbons (mesitylenes and dotriacontane) appear in figure 17 as a function of temperature. Here boundary film failure occurs at the melting point of each hydrocarbon. Although data for only two hydrocarbons are shown in figure 17, the same phenomenon occurred for several other compounds. Obviously, the films of these nonpolar materials, which are not chemically bound to the copper surface, provide little protection in the liquid state.

In contrast, chemisorption of fatty acids on reactive metals yields failure temperature based on the softening point of the soap rather than the melt-

ing point of the parent fatty acid. Examples of transition temperatures for

several fatty acids appear in figure 18 (ref. 18).

Chemically reacted inorganic surface films such as oxides and sulfides do not have failure transitions that correlate with their melting points. These materials often have very high melting points (>1000°C) and other factors (such as decomposition or physical removal) may limit their effectiveness at temperatures well below their melting point.

Shear Strength

The shear strength of a boundary lubricating film should be directly reflected in the friction coefficient. In general, this is true with low shear strength soaps yielding low friction while high shear strength salts yield high friction (ref. 5). However, the important parameter in boundary friction is the ratio of the shear strength of the film to that of the substrate (ref. 5). This relationship is illustrated in figure 19. Shear strength is also affected by both pressure and temperature. For example, shear stress as a function of load (pressure) for steeric acid is shown in figure 20 (ref. 19). A compilation of similar data for inorganic compounds appears in reference 20.

Boundary Film Thickness

Boundary film thicknesses can vary from a few angstroms (adsorbed gas) to thousands of angstroms (chemical reaction film). The effect of thickness on friction has been discussed in detail by Kragelskii (ref. 21). In general, as the thickness of a boundary film increases, the coefficient of friction decreases (fig. 21(a)). However, continued increases in thickness may result in an increase in friction (fig. 21(b)). This figure has the general form of the familiar Stribeck-Hersey curve (fig. 1). Another point of interest: shear strength of all boundary films decreases as their thickness increases, which may be related to the above.

For physically adsorbed or chemisorbed films, surface protection is usually enhanced by increasing film thickness (ref. 18). The frictional transition temperature of multilayers also increases with increasing number of layers (ref. 3).

For thick chemically reacted films there is an optimum thickness for minimum wear which depends on conditions. The relationship between wear and lubricant (or additive) reactivity is shown in figure 22. Here, if reactivity is not great enough to produce a thick enough film, adhesive wear occurs. On the other hand, if the material is too reactive, very thick films are formed and corrosive wear ensues. Lubricant or additive reactivity is also a function of temperature (fig. 23) (ref. 22) and concentration (fig. 24) (ref. 7).

Effect of Operating Variables on Friction

Load

As mentioned in the earlier discussion on the Stribeck-Hersey curve (fig. 1), in the boundary lubrication regime, the coefficient of friction is essentially constant with increasing load. This is a statement of Amonton's law which says that the coefficient of friction is independent of load. This law is amazingly well obeyed for most systems if there is no boundary film

failure. This is illustrated in figure 25 (ref. 23) for copper surfaces lubricated with two fatty acids. At loads (>50 g) the coefficient of friction is essentially constant. The increasing friction at decreasing loads is probably related to molecular orientation effects and the fact that film penetration does not occur.

Speed

In general, in the absence of viscosity effects, friction changes little with speed over a sliuing speed range of 0.005 1.0 cm/sec (ref. 4). Where viscosity effects do come into play, two types of behavior are observed. These are illustrated in figure 26 (ref. 24). Here, relatively nonpolar materials such as mineral oils show a decrease in friction with increasing speed while polar fatty acids show the opposite trend. In addition, the mineral oil behavior is usually associated with stick-slip phenomena. This is of practical importance since a good boundary lubricant does not lead to stick-slip behavior.

At high speeds, viscous effects will be present and increases in friction are normally observed (fig. 27) (ref. 25). This portion of the friction curve is analgous to the rising portion of the Stribeck-Hersey curve (fig. 1) as one approaches hydrodynamic lubrication.

Temperature

It is impossible to generalize about the effect of temperature on boundary friction. So much depends on the other conditions and the type of materials present. Temperature can cause disruption, desorption, or decomposition of boundary films. It can also provide activation energy for chemisorption or chemical reactions. The frictional transition temperatures of figure 18 show the effect of temperature on the melting of the chemisorbed fatty acids.

Atmosphere

The presence of oxygen and water vapor in the atmosphere can greatly affect the chemical processes that occur in the boundary layer. These processes can, in turn, affect the friction coefficient. The importance of atmospheric and adsorbed oxygen is illustrated in figure 28 (ref. 26). Here, the "EP" activity of tricresylphosphate (TCP) is totally absent in a dry nitrogen atmosphere. In contrast, normal "EP" activity is present in dry air.

Effect of Operating Variables on Wear

Load

It is generally agreed that wear increases with increasing load but no simple relationship seems to exist. This refers to the situation where no transition to severe wear has occurred. At this point, a discontinuity on wear versus loan occurs which is illustrated in figure 2. Figure 29 illustrates the increasing load (ref. 4).

Speed

For practical purposes, wear rate in the boundary lubrication regime is essentially independent of speed. Obviously, this does not hold if one moves

into the EHD regime with increasing speed. This also assumes no boundary film failure due to contact temperature rise. An example of wear rate as a function of sliding speed appears in figure 30 (ref. 28). These data indicate that fluid film effects are negligible only at 25 and 50 rpm and a 1 kg load.

Temperature

As was the case for friction, there is no way to generalize the effect of temperature on wear. The same statements that pertain to friction also pertain to wear. A good example of the effect of temperature on wear is presented in figure 23.

Atmosphere

The effects of atmospheric oxygen and moisture on wear has been studied by many investigators. Oxygen has been shown to be an important ingredient in boundary lubrication experiments involving load carrying additives (refs. 4, and 29 to 33). For example, the presence of oxygen or moisture in the test atmosphere has a great effect on the wear properties of lubricants containing aromatic species (figs. 31 and 32) (refs. 27 and 33).

Additive Behavior of Boundary Lubricated Systems

In discussing figure 2, it was stated that the boundary lubrication regime could be extended to higher loads by proper formulation of the lubricant with additives. A discussion of the variety of boundary additives is outside the scope of this paper. However, the general behavior of the two common types of boundary additives, namely, antiwear and "EP", is illustrated in figure 33 (ref. 34). In figure 33 wear rate (K) is plotted as a function of load (F). There is a wear transition when boundary film failure occurs. The presence of an antiwear additive reduces wear (ΔK) but may have little or no effect on the wear transition load. On the other hand, an "EP" additive yields an increase in the load carrying capacity (ΔF) with little or no effect on the wear rate below the original base oil wear transition.

The most common antiwear additives are those which contain the element phosphorus. Typical examples include the metal dialkyldithiophosphates, organic phosphates and phosphites. "EP" additives include compounds containing sulfur and chlorine. A review of these two additive classes appears in reference 35.

CONCLUDING REMARKS

In conclusion, the boundary lubrication regime has been shown to be a complex arena of a variety of competing chemical and physical processes. The ultimate understanding of this regime will come when these processes and their interrelationships are completely identified.

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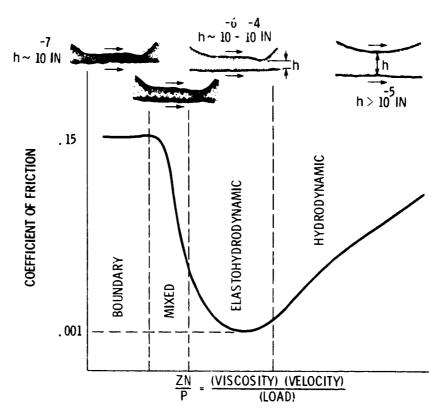


Figure 1. - Coefficient of friction as a function of speed-velocity-load parameter (Stribeck-Hersey curve) (ref. 1).

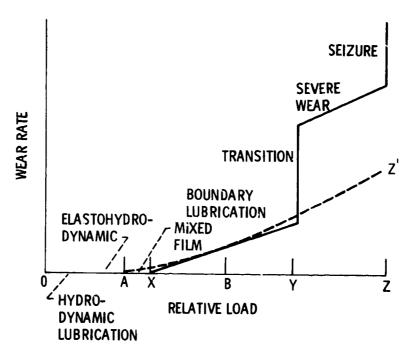


Figure 2. - Wear rate as a function of relative load depicting the various regimes of lubrication (ref. 8).

OIL INLET

OIL SAMPLE

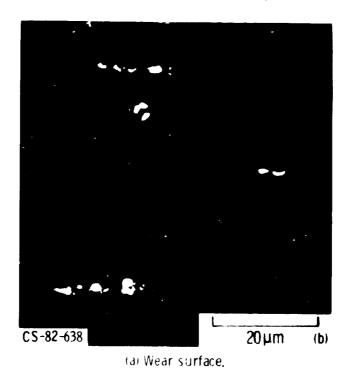
ENTRY POSITION

(55-56 mm)

MAGNET

Figure 3. - Ferrograph analyzer.

40 µm (a)

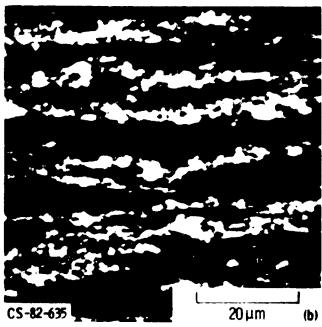


(b) Wear particles (ref. 9).

Figure 4. - Hydrodynamic or elastohydrodynamic lubrication regime.

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- 40μm (a



(a) Wear surface.

(b) Wear particles (ref. 9).

Figure 5. - Boundary lubrication regime.

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5 μm CS-77-286

Figure 6. - Normal rubbing wear particles (from ref. 11).

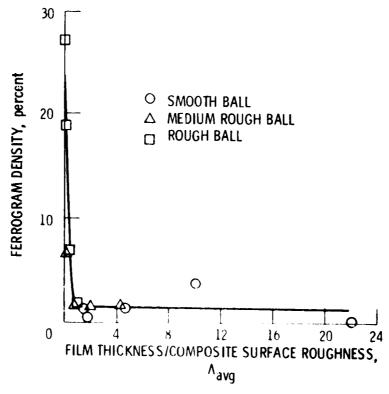


Figure 7. - Ferrogram density versus average Λ ratio (ref. 12).

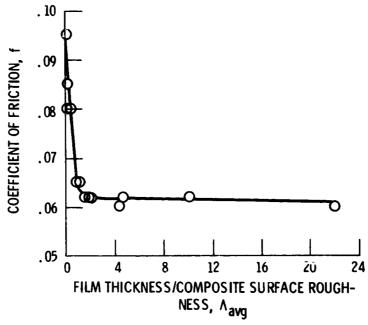


Figure 8. - Friction versus average Λ ratio (ref. 12).

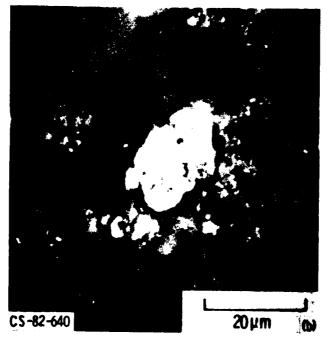
40 µm C\$-639 20 µm

(a) Wear surface.
(b) Wear particles (ref. 9).

Figure 9. - Transition to severe wear.

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40 µm (a)

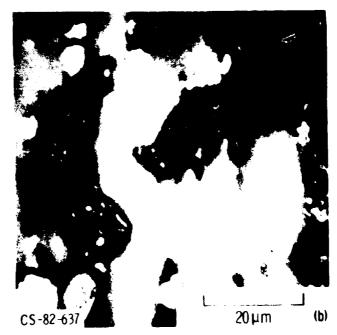


(a) Wear surface.
(b) Wear particles (ref. 9).

Figure 10. - Severe wear regime-mild oxidative wear.

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40μm (a)

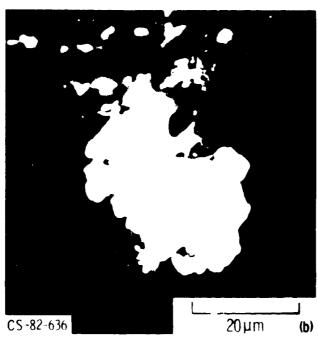


(a) Wear surface.(b) Wear particles (ref. 9).

Figure 11. - Severe wear regime-severe oxidative wear.

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L 40 μm (a)



(a) Wear surface.
(b) Wear particles (ref. 9).

Figure 12. - Transition to seizure.

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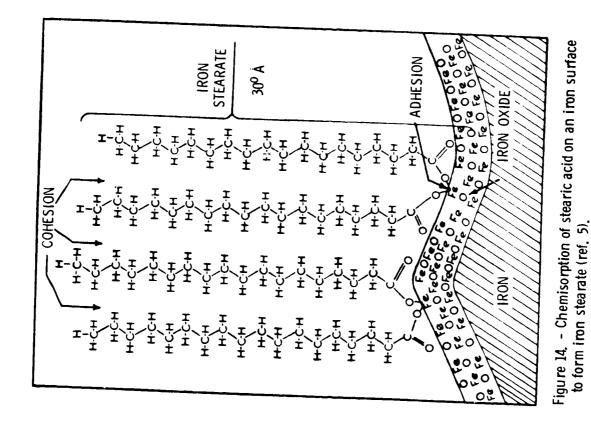


Figure 13. - Physical adsorption hexadecanol (ref. 5).

UNREACTIVE METAL

ADHESION

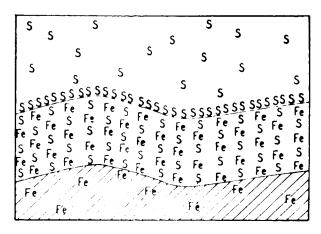


Figure 15. - Inorganic film formed by reaction of sulfur with iron to form iron sulfide (ref. 5).

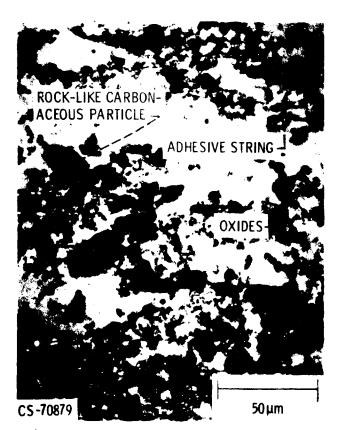


Figure 16. - Photomicrograph of the wear debris generated by a polyphenyl ether at 100° C in dry test atmosphere of 1 percent oxygen and 99 percent nitrogen (by volume)(ref. 15).

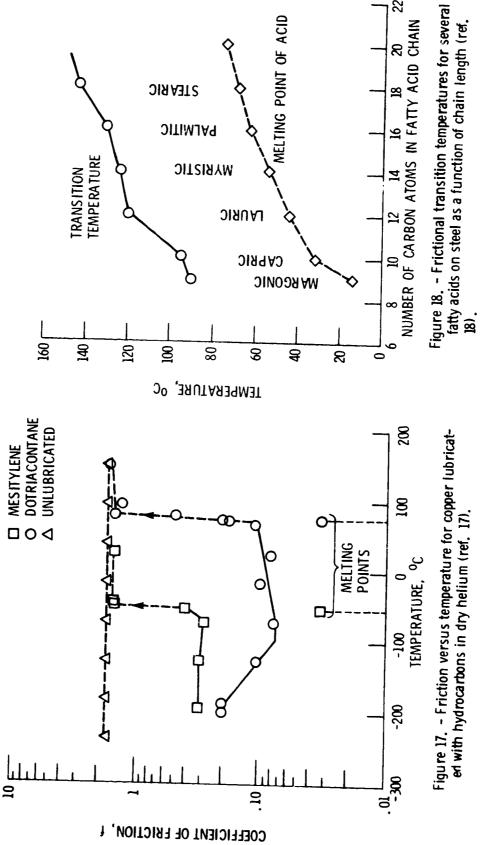


Figure 17. - Friction versus temperature for copper lubricated with hydrocarbons in dry helium (ref. 17).

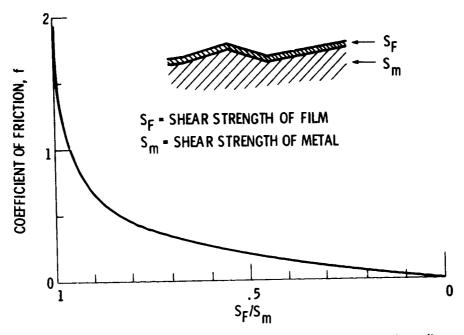


Figure 19. - Friction as a function of the ratio of shear strengths of film and metal (ref. 5).

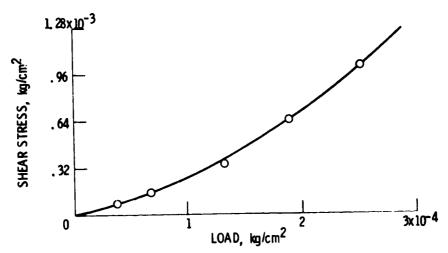


Figure 20. - Shear stress as a function of load for a thin layer of solid stearic acid (ref. 19).

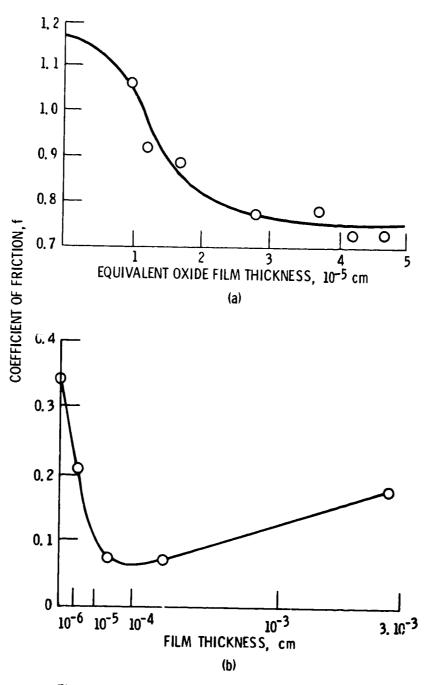


Figure 21. - Relationship between friction and thickness of surface films: (a) coefficient of friction against oxide film thickness on copper; (b) coefficient of friction against thickness of indium film (ref. 21).

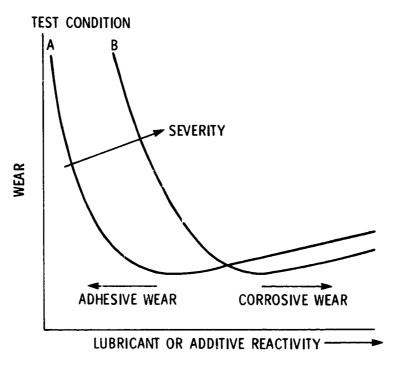


Figure 22. - Relationship between wear and lubricant reactivity (ref. 7).

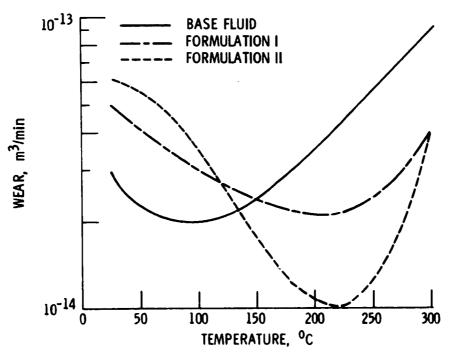


Figure 23. - Wear versus temperature for various C-ether formulations (ref. 22).

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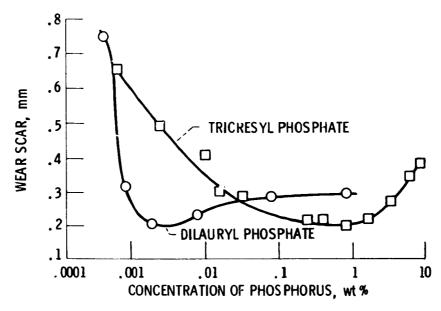


Figure 24. - Wear versus additive concentration from four-ball tests (ref. 7).

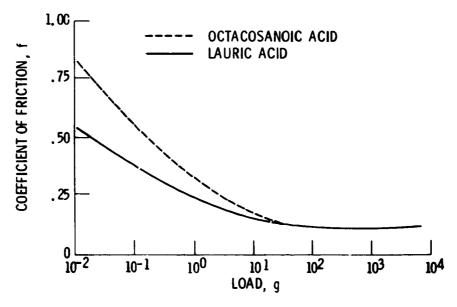


Figure 25. - Friction versus load for copper lubricated with fatty acids (ref. 23).

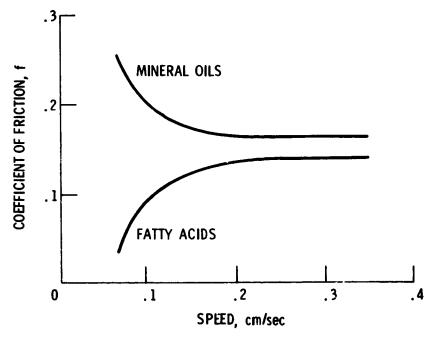


Figure 26. - Friction versus speed (ref. 24).

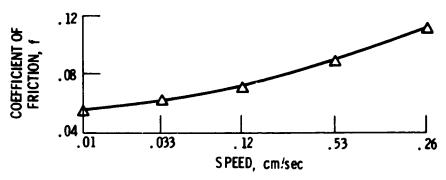


Figure 27. - Friction versus speed for steel/bronze lubricated with oleic acid (ref. 25).

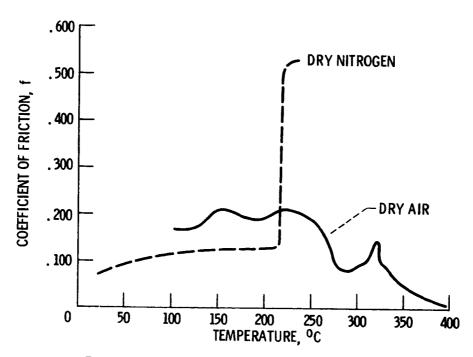


Figure 28. - Friction versus temperature for pure tricresyl phosphate on M-50 steel. (Ref. 26)

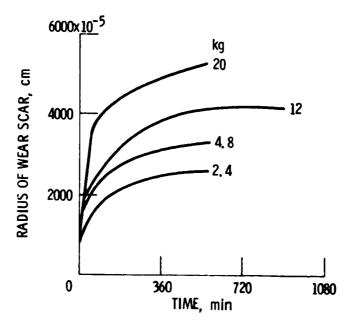


Figure 29. Radius of wear scar as a function of time for several loads. (Ref. 4)

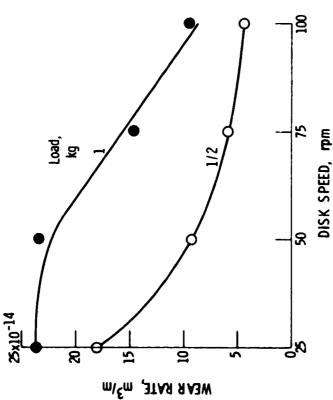
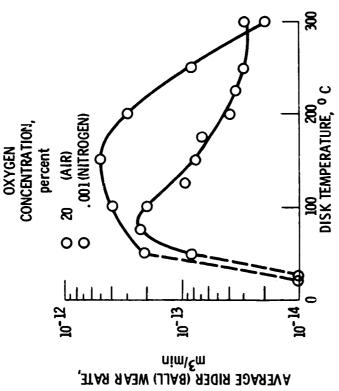


Figure 30. - Effect of disk speed on rider wear rate at dry air; disk temperature, 200 C; pure iron rider two loads with ester-base lubricant. Atmosphere, on M-50 (ref. 28).



concentrations. Specimen material, CVM M-50 steel; load, 1 kilogram; sliding speed, 17 me-Figure 31. - Average rider (ball) wear as a function of disk temperature with a five-ring polyphenyl ether in atmospheres with two oxygen ters per minute (100 rpm); test duration, 25 minutes. (Ref. 33)

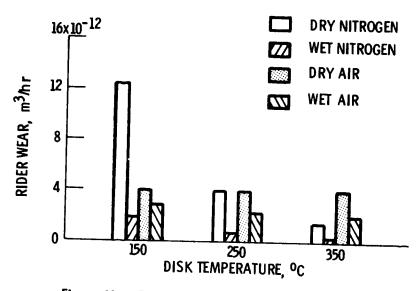


Figure 32. - Rider wear for polyphenyl ether in wet and dry nitrogen and in wet and dry air at disk temperatures of 150°, 250°, and 350° C. (Ref. 27)

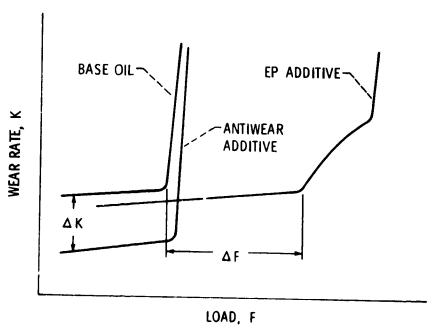


Figure 33. - Wear behavior of boundary-lubrication systems (ref. 34).

						
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16.	A review of the various lubrication regimes, with particular emphasis on boundary lubrication, is presented. The types of wear debris and extent of surface damage is illustrated for each regime. The role of boundary surface films along with their modes of formation and important physical properties are discussed. In addition, the effects of various operating parameters on friction and wear in the boundary lubrication regime are considered.					
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